Effect of the Complexation on Solubility of Pu(IV) in Aqueous Carbonate System

By Tetsuji Yamaguchi, Yoshiaki Sakamoto and Toshihiko Ohnuki

Department of Environmental Safety Research, Japan Atomic Energy Research Institute, Tokai, Ibaraki, 319-11, Japan

Solubility / Plutonium / Plutonium hydroxy-carbonates / Plutonium hydrous oxide / Stability constant
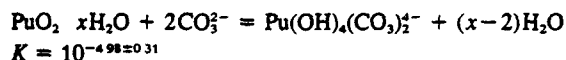
Abstract

Solubility of Pu(IV) was measured over a total carbonate concentration range of 10^{-4} to 10^{-1} M at room temperature (20−25 °C) and I = 0 1 Since carbonate was not detected in the solid phase, the solubility controlling solid was assumed to be a hydrous oxide, $PuO_2 \cdot xH_2O$ A limit of the equilibrium constant of the exchange reaction between $PuO_2 \cdot xH_2O$ and a carbonate solid phase, $PuOCO_3 \cdot xH_2O$, was estimated as

$$PuO_2 \cdot xH_2O + CO_3^{2-} + H_2O = PuOCO_3 \cdot xH_2O + 2OH^-$$
$$K < 10^{-6.7}$$
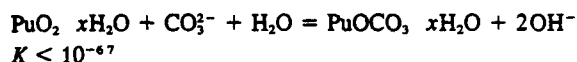
The measured solubility was proportional to the square of the bicarbonate concentration at the pH range of 9 4−10 1 This result was interpreted by

$$PuO_2 \cdot xH_2O + 2HCO_3^- = Pu(OH)_2(CO_3)_2^{2-} + xH_2O$$
$$K = 10^{-2.7\pm0.5}$$
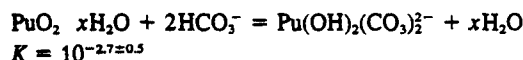
At pHs 12 and 13 where carbonate ion is dominant,

$$PuO_2 \cdot xH_2O + 2CO_3^{2-} = Pu(OH)_4(CO_3)_2^{4-} + (x-2)H_2O$$
$$K = 10^{-4.98\pm0.31}$$

is the predominant reaction

1. Introduction

The solubility of radionuclides is one of the more important parameters controlling their release from a deep underground radioactive waste repository Prediction of the solubility requires a knowledge of all relevant species present in solution Complexation of metal ions with ligands may stabilize them in natural waters, and thus can control the speciation and solubility of radionuclides of interest Because of their strong tendency of complexation, carbonate or bicarbonate ions are likely to be some of the most significant ligands to be considered [1, 2] Therefore, a clearer understanding of the effect of carbonate complexation on solubility is needed

The complexation of Pu(IV) by carbonate has been studied [3, 4, 5] Moskvin and Gel'man [3] showed that the carbonate complex species, $Pu(CO_3)^{2+}$, was present in 0 36−3 6 M K_2CO_3 solutions Their work, however, has been reviewed critically [5, 6], and some misunderstandings have been pointed out. Kim *et al* [4] suggested that $Pu(CO_3)_x^{4-2x}$ (x = 1−5) are the dominant aqueous species with $Pu(OH)_2CO_{3(s)}$ as the solubility-controlling solid in $NaClO_4/NaHCO_3/Na_2CO_3$ solutions at pH > 8 and I = 1 0 Pratopo *et al* [7] studied the carbonate complexation of Np(IV) by a solubility method and suggested the presence of $Np(OH)_2(CO_3)_2^{2-}$ (or $Np(OH)_4(HCO_3)_2^{2-}$) and $Np(OH)_4(CO_3)_2^{4-}$ They also analyzed the concentration of U(IV) in Swedish ground-water by taking into account the presence of $U(OH)_2(CO_3)_2^{2-}$

Despite the fact that the chemical properties of tetravalent actinides are expected to be similar, there are certain discrepancies in their complexation data Considering the critical role of carbonate complex species in safety assessment of radioactive waste disposal, much more reliable information is necessary In the present study, the Pu(IV) solid phase was characterized and the dependence of Pu(IV) solubility on carbonate-bicarbonate concentration was studied at the pH range of 9 4−13

2 Experimental

2 1 Preparations

Sample solutions were prepared from reagent grade chemicals (Wako Pure Chemical Ind , Ltd , Tokyo) and deionized water (Milli-Q System, Millipore) The isotopic composition of the plutonium was 0 0031% ^{238}Pu, 97 41% ^{239}Pu, 2 56% ^{240}Pu and 0 026% ^{241}Pu Plutonium was chemically purified by anion exchange The eluted Pu in hydrochloric acid was converted to Pu(IV) as a nitrate and prepared as a 1 8×10^{-4} M solution in 10 M HNO_3

2 2 Procedures

An aliquot of the Pu(IV) stock solution was added to a 20 ml solution containing KCl, K_2CO_3 and KOH in a polypropylene tube The initial concentrations of Pu(IV), K^+ and total carbonate (C_t) in the sample solution were typically 1 3×10^{-6}, 0 1 and 10^{-4}−10^{-1} M, respectively The pH was adjusted to values between 9 4 and 13 0 by adding dilute KOH A 0 1 ml volume of 0 1 M $NaNO_2$ solution was added to maintain the Pu in the tetravalent state The samples were sealed and stored for 2 weeks in air at room temperature (20−25 °C)

After two weeks, the pH and Eh of the sample solutions were measured with a Ag/AgCl electrode

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and a Pt/AgCl electrode, respectively The electrode was calibrated with pH buffer solutions (pH = 6 86 and 9 18) and a ORP standard (95 mV against the reference electrode) The total carbonate concentration was measured with CO_2 electrode (TOA Electronics Ltd. Japan, type CE-235, detection limit $4 0\times10^{-5}$ M) The electrode had been calibrated with a $KHCO_3$ solution using the same procedure as for the measurement of the carbonate concentration The micro-centrifuge system (Millipore) was used to effect the separation processes A 0 5 ml aliquot of the sample solution was filtered through 0 45 μm durapore (PVDF) and 10,000 NMWL (nominal molecular weight limit) poly sulphur filters that had been rinsed with blank solution The average pore size was estimated to be about 450 nm and 3 nm, respectively Plutonium remaining on filters was redissolved by passing 1 M HNO_3 through the filters The concentration of Pu was measured with α-spectroscopy after evaporating 50 μl of the final filtrate on a stainless steel planchet

The oxidation state of the Pu was determined by TTA extraction [7−9] A 100 μl aliquot of the final filtrate was acidified with 1 ml of 1 M HCl An equal volume of 0 4 M TTA in xylene was added and the mixture was shaken for 10 min This method was validated using K_2CO_3 solutions spiked with a Pu(IV) stock solution and a Pu(VI) perchloric acid solution and by reacidifying these solutions (Pu concentration = 10^{-8} M) within 10 min for TTA extraction

Plutonium solid that had formed in a few samples was used for characterization The initial concentrations of Pu(IV) and C_t in these samples were $1 0\times10^{-4}$ M and $0 01−0 1$ M, respectively, and the pH was 9 65−9 85 and 12 The solid phase was trapped on a 0 45 μm filter, rinsed 3 times with 1 ml of deionized water and redissolved in 2 ml of 1 M H_2SO_4 The concentrations of carbonate and plutonium dissolved from the solid were measured with the CO_2 electrode and α-spectrometer, respectively To prevent the disturbance on the carbonate measurement by acidic gas, a non-volatile acid (H_2SO_4) was used to dissolve the solid The electrode was calibrated with a $KHCO_3$ solution using 1 M H_2SO_4 as an acidifier In this case, the detection limit was 6×10^{-5} M

To check the methods used to characterize the solid material, a preliminary test was carried out using cobalt (Co^{2+}) in place of plutonium Cobalt was chosen because both hydroxide and carbonate precipitates can be readily prepared A cobalt precipitate was prepared from $CoCl_2$ solution with an addition of $NaHCO_3$ at pH = 8 0 and C_t = 0 1 M The amount of cobalt was varied from 24 to 120 μg Precipitates were also prepared in 0 1 M Na_2CO_3 at pH = 11 0 and 0 1 M $NaClO_4$ at pH = 11 0 for comparison

3. Results and discussion

3 1 Cobalt

Cobalt forms $Co(OH)_{2(s)}$ ($\log K_{sp}$ = −15 2 [10]) in alkaline solutions and $CoCO_{3(s)}$ ($\log K_{sp}$ = −9 98

Table 1 Carbonate content analysis for cobalt precipitates

Co μg	Condition of precipitation		Solid	[Co][a] mM	Σ[CO₂][b] mM
24	0 1M $NaHCO_3$	(pH≈8)	$CoCO_3$	0 2	0 23
48	0 1M $NaHCO_3$	(pH=8)	$CoCO_3$	0 4	0 40
72	0 1M $NaHCO_3$	(pH≈8)	$CoCO_3$	0 6	0 66
96	0 1M $NaHCO_3$	(pH=8)	$CoCO_3$	0 8	0 84
120	0 1M $NaHCO_3$	(pH=8)	$CoCO_3$	1 0	0 98
120	0 1M Na_2CO_3	(pH=11)	$Co(OH)_2$	1 0	0 09[c]
120	0 1M Na_2CO_3	(pH=11)	$Co(OH)_2$	1 0	0 11[c]
120	0 1M Na_2CO_3	(pH=11)	$Co(OH)_2$	1 0	0 11[c]
120	0 1M $NaClO_4$	(pH=11)	$Co(OH)_2$	1 0	<0 06
120	0 1M $NaClO_4$	(pH=11)	$Co(OH)_2$	1 0	<0 06
120	0 1M $NaClO_4$	(pH=11)	$Co(OH)_2$	1 0	<0 06

[a] Assuming that all the cobalt was dissolved in 1 M H_2SO_4.
[b] Total carbonate concentration measured in 1 M H_2SO_4
[c] About 0 1 mM carbonate was detected, which is likely due to incomplete rinsing of the solid

Table 2 Carbonate content in Pu solid phase

Pu μg	Condition of precipitation		[Pu] mM	[CO₂][a] mM
500	0 01M $KHCO_3$	(pH=9 65)	1 0	<0 1
500	0 03M $KHCO_3$	(pH=9 82)	1 0	<0 1
500	0 1 M $KHCO_3$	(pH=9 85)	1 0	<0 1
500	0 05M K_2CO_3	(pH=12 0)	1 0	<0 1

[a] The detection limit of this measurement in carbonate and bicarbonate solution is 0 1 mM (see text)

[11]) in carbonate solutions Cobalt carbonate may be formed in the $NaHCO_3$ solution (pH = 8 0) by the following reaction

$$Co^{2+} + HCO_3^- = CoCO_{3(s)} + H^+ \tag{1}$$

Cobalt hydroxide may be formed in the Na_2CO_3 (pH = 11 0) and 0 1 M $NaClO_4$ solutions (pH = 11 0) by the following reaction

$$Co^{2+} + 2OH^- = Co(OH)_{2(s)} \tag{2}$$
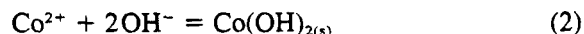
The results of the carbonate concentrations for the cobalt precipitates are shown in Table 1 The measured carbonate molarity at pH = 8 is almost equal to that of cobalt At pH = 11, on the other hand, the measured carbonate molality is much less than that of the cobalt This indicates that carbonate determination in precipitates can be used to determine whether the plutonium precipitate is carbonate or not The error of measurement is about 10% and is possibly the result from incomplete separation and rinsing of the solid The results for the three runs at pH 11 in Na_2CO_3 are higher than those in $NaClO_4$ and may be due to adsorption of carbonate on the solid and incomplete rinsing of the solid Hence, detection limit of this determination is considered to be 0 1 mM

3 2 Characterization of the plutonium solid phase

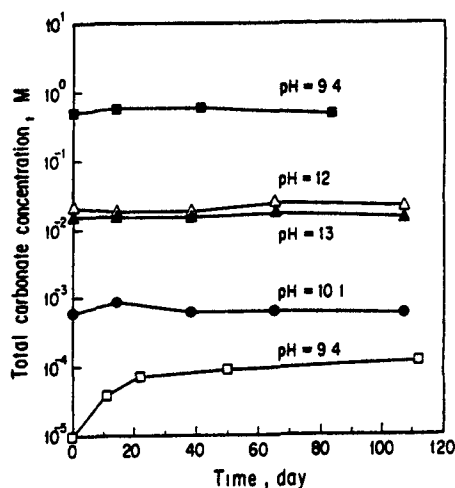The carbonate concentrations for the Pu(IV) solid phase are shown in Table 2 Even in the 0 1 M $KHCO_3$

Fig. 1 Time dependence of total carbonate concentrations for $10^{-5}-0.5$ M $KHCO_3/K_2CO_3$ solutions in the pH range of $9.4-13$

Fig 2 Measured redox potential versus pH for the Pu(IV) carbonate-bicarbonate solutions with $NaNO_2$ The line corresponds to Eq (4)

solution, the carbonate content was below the detection limit (0.1 mM) The virtual absence of carbonate suggests the formation of hydrated oxide $PuO_2 \cdot xH_2O$

Our results do not agree with earlier predictions [4, 5] suggesting the transformation of solid species from oxide to hydroxycarbonate in solutions of $> 10^{-4}$ M carbonate In the present study, the mole fraction of hydrated oxide and hydroxycarbonate were > 0.9 and < 0.1, respectively The equilibrium constant of the transformation reaction

$$PuO_2 \cdot xH_2O + CO_3^{2-}$$
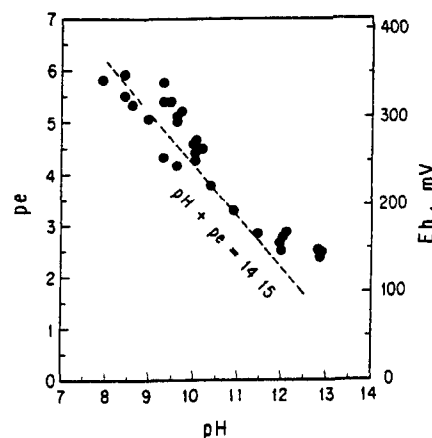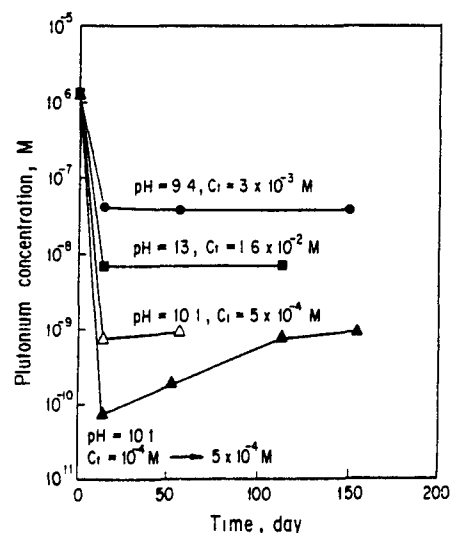$$+ H_2O = PuOCO_3 \cdot xH_2O + 2OH^- \quad (3)$$
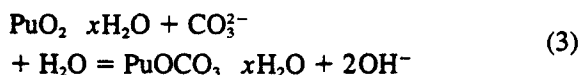
was estimated to be $K < 10^{-6.7}$ This calculation was based on the assumption that the ratio of the mole fraction between the solid phases was equal to their activity ratio The solubility product of $PuO_2 \cdot xH_2O$ at $I = 0.1$ was estimated to be $\log K_{sp} = -54.70$ using the Davies equation [12] A solubility product, K_{sp}, of $>10^{-48.0}$ was estimated for $PuOCO_3 \cdot xH_2O$

3.3 Stability constant of Pu(IV) hydroxycarbonate complexes

Carbonate concentrations in the range of $10^{-4}-0.5$ M were kept approximately constant for about 100 days under the experimental conditions as shown in Fig 1 A sample of the concentration as low as 10^{-5} M was affected by the atmospheric CO_2

Figure 2 shows the redox potential of the sample solutions at different pHs The following reaction is likely to control the redox condition of the sample solutions

$$1/2NO_2^- + 1/2H_2O = 1/2NO_3^- + H^+ + e^- \quad (4)$$
$$K = 10^{-14.15}$$
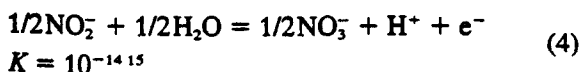
Pu(IV) is extracted by TTA while other oxidation states remain in the aqueous phase [9] in 1 M HCl

Fig 3 Equilibration of plutonium(IV) concentrations for $10^{-4} - 1.6 \times 10^{-2}$ M $KHCO_3/K_2CO_3$ solutions in the pH range of $9.4-13$, O, ■, △ oversaturation, ▲ undersaturation

The extraction of Pu(IV) from carbonate solution was $(92.9\pm2.4)\%$, while that of Pu(VI) was less than 0.3% was determined from the validation experiment More than 90% of the Pu was extracted from the sample solutions under the condition indicating that the Pu was mainly in the tetravalent state, although a 10% uncertainty exists

A series of solubility measurements was carried out at pHs 9.4, 10.1, 13 from the direction of oversaturation to determine the time required for equilibrium to be reached As shown in Fig 3, the Pu concentrations reach equilibrium within the first 14 days from the direction of oversaturation The total carbonate concentration of a sample of pH 10.1 was increased at the 14th day by adding $KHCO_3$ and K_2CO_3 The solid phase began to dissolve and took 100 days to reach a new equilibrium concentration This suggests that longer equilibration times are needed from the undersaturation direction than from the oversaturation direc-
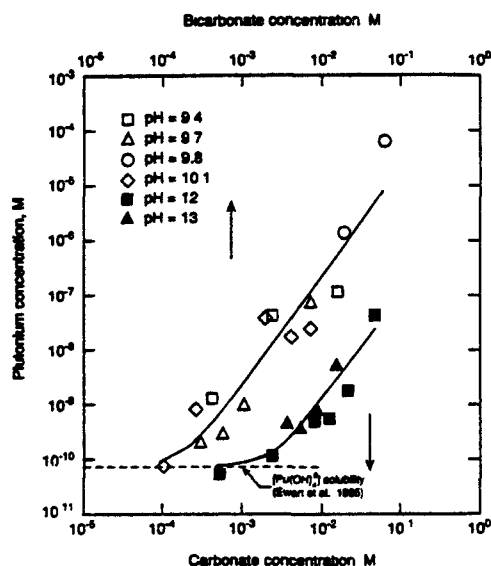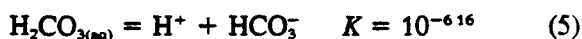
Fig 4 Effect of bicarbonate concentration on solubility of Pu(IV) at pH = 9 4, 9 7, 9 8 and 10 1, and effect of carbonate concentration at pH 12 and 13 The solid curves show the results of the least-squares fitting The dashed line shows the contribution of Pu(OH)$^0_4$

tion Although the equilibrium from the undersaturation direction was also investigated at pH = 13, the conccentration was still increasing after 200 days The equilibrium was not confirmed because Eh and total carbonate concentration were significantly affected by atmospheric O_2 and CO_2 An equilibration period of 14 days and the oversaturation direction were chosen for the present study Considering that the solid phase will proceed to crystallize, the equilibrium state discussed here may be a pseudo equilibrium state

The measured solubility of Pu(IV) is shown in Fig 4 In low carbonate solutions, an aqueous neutral species of Pu(OH)$^0_4$ is dominant Its solubility was reported by Ewart et al [13] The solubility measured at $C_t > 10^{-4}$ M is far higher than that of Pu(OH)$^0_4$, which is due to complexation Although the chloride anion is the main anionic species in the sample solutions, the complex formation of Pu(IV) by Cl$^-$ is negligible according to the predicted formation constant (log$\beta_{PuCl^{3+}}$ = 1 33 [14]) Carbonate and bicarbonate concentrations were calculated from C_t and pH using the following equilibrium constants [15] at I = 0 1

$$H_2CO_{3(aq)} = H^+ + HCO_3^- \quad K = 10^{-6\ 16} \quad (5)$$

$$HCO_3^- = H^+ + CO_3^{2-} \quad K = 10^{-10\ 00} \quad (6)$$

$$H_2O = H^+ + OH^- \quad K = 10^{-13\ 78} \quad (7)$$

Because the Pu fraction remaining on the filter was one order of magnitude lower than that in the final filtrate, the size of main Pu species in sample solutions was less than 3 nm The data analysis presented in this paper is based on two assumptions (a) the thermodynamic activity of the solid is the same for all carbonate and bicarbonate concentrations, and (b) bi-nuclear or polynuclear species are not involved

Because bicarbonate ion is dominant over the pH range of 9 4–10 1, the measured Pu concentrations are plotted versus [HCO$_3^-$] The Pu solubility depends on the bicarbonate concentration over this pH range, log[Pu(IV)] is proportional to log[HCO$_3^-$] with the slope of 2 Hence, we considered the following reaction

$$PuO_2 \ xH_2O + 2HCO_3^- = Pu(OH)_n(CO_3)_2^{-n} \\ + (2-n)OH^- + xH_2O \quad (8)$$
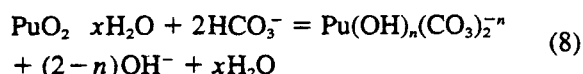
To determine the value for n, the slope of log([Pu(OH)$_n$(CO$_3$)$_2^{-n}$/[HCO$_3^-$]^2) against log[OH$^-$] was calculated to be 0 23±0 57 The best fit for this data is $n = 2$ although a certain error ($n = 2\ 23±0\ 57$) is associated with this fit The Pu concentration in bicarbonate solution is given by the sum of [Pu(OH)$^0_4$] (= $10^{-10\ 14}$ M [13]) and [Pu(OH)$_2$(CO$_3$)$_2^{2-}$] A least-squares method gives the equilibrium constant of $10^{-27±0\ 5}$ for Eq (9)

$$PuO_2 \ xH_2O + 2HCO_3^- = Pu(OH)_2(CO_3)_2^{2-} \\ + xH_2O \quad (9)$$
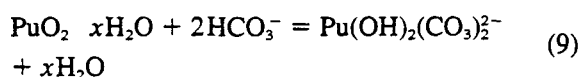
Carbonate ion dominates in the higher pH range, in place of bicarbonate At pH = 12 and 13, the solubility at [CO$_3^{2-}$] $> 10^{-3}$ M is proportional to the square of the carbonate concentrations and can be estimated by reaction (10)

$$PuO_2 \ xH_2O + 2CO_3^{2-} = Pu(OH)_4(CO_3)_2^{4-} \\ + (x-2)H_2O \quad (10)$$
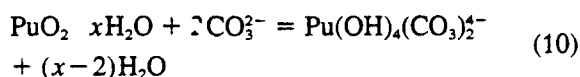
The Pu concentration in the carbonate solution is given by the sum of [Pu(OH)$^0_4$] and [Pu(OH)$_4$(CO$_3$)$_2^{4-}$] A least-squares method gives an equilibrium constant of $10^{-4\ 98±0\ 31}$ for Eq (10) Since the data at pH 12 are nearly identical to those at pH 13, the following pH-dependent reaction was ruled out

$$PuO_2 \ xH_2O + 2CO_3^{2-} = Pu(OH)_3(CO_3)_2^{3-} \\ + OH^- + (x-2)H_2O \quad (11)$$
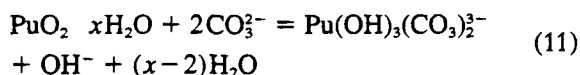
Together with the solubility products of PuO$_2$ xH$_2$O, the stability constants of Pu(OH)$_2$(CO$_3$)$_2^{2-}$ and Pu(OH)$_4$(CO$_3$)$_2^{4-}$ were calculated to be $10^{44\ 2±0\ 6}$ and $10^{49\ 72±0\ 48}$, respectively The stability constants of the hydroxycarbonate complex species are tabulated in Table 3

The present interpretation for Pu(IV) carbonates is similar to that for Np(IV) carbonates [7] The formation of Pu(CO$_3$)$_x^{4-2x}$ ($x = 1-5$) and Pu(OH)$_2$CO$_{3(s)}$, both of which have been predicted by Kim et al [4] and Lierse [5], were not consistent with our experimental results Their solubility in the pH range of 9 to 11 can be fitted with Eq (9) as well as their interpretation in which the formation of Pu(CO$_3$)$_3^{2-}$ was taken into account Their solubility in higher pH range was proportional to the square of the carbonate concentration and can be fit with Eq (10) as well as their interpretation in which the formation of Pu(CO$_3$)$_x^{4-2x}$ $x = 4, 5$ was taken into account The Eh-pH diagram calculated by using the present data and data compiled

Table 3 Equilibrium constants of An(IV) hydrolysis and carbonate species

Reaction	Ionic strength	log K	log stability constant of product*
$PuO_2 \cdot xH_2O + 2HCO_3^- = Pu(OH)_2(CO_3)_2^{2-} + xH_2O$	0 1	$-2\ 7\ \pm 0\ 5$	44 2 $\pm 0\ 6$
$PuO_2 \cdot xH_2O + 2CO_3^{2-} = Pu(OH)_4(CO_3)_2^{4-} + (x-2)H_2O$	0 1	$-4\ 98 \pm 0\ 31$	49 72$\pm 0\ 48$
$Pu(OH)_{4(s)} = Pu(OH)_4^0$	0	$-10\ 14 \pm 0\ 28$ [13]	46 71$\pm 0\ 46$
	0 1	$-10\ 14 \pm 0\ 28$	44 56$\pm 0\ 46$
$Pu^{4+} + 4OH^- + (x-2)H_2O = PuO_2 \cdot xH_2O_{(am)}$	0	56 85$\pm 0\ 36$ [12]	$-$
	0 1	54 70$\pm 0\ 36^b$	$-$
$Pu^{4+} + 2OH^- + CO_3^{2-} + (x-1)H_2O = PuOCO_3 \cdot xH_2O$	0 1	$<48\ 0$	$-$
$Np(OH)_{4(am)} + 2HCO_3^- = Np(OH)_2(CO_3)_2^{2-} + 2H_2O$	0 3	$-0\ 35 \pm 0\ 33$ [7]	43 1 $\pm 0\ 4$
$Np(OH)_{4(am)} + 2CO_3^{2-} = Np(OH)_4(CO_3)_2^{4-}$	0 3	$-1\ 43 \pm 0\ 33$ [7]	50 5 $\pm 0\ 4$
$Np(OH)_{4(am)} = Np(OH)_4^0$	0 3	$-8\ 5\ \pm 0\ 1$ [16]	43 4 $\pm 0\ 3$
$Np^{4+} + 4OH^- + (x-2)H_2O = NpO_2 \cdot xH_2O_{(am)}$	0	54 5 $\pm 0\ 3$ [12]	$-$
	0 3	51 9 $\pm 0\ 3^b$	$-$
$U(OH)_{4(am)} + 2HCO_3^- = U(OH)_2(CO_3)_2^{2-} + 2H_2O$	varied	$> -2\ 44$ [7]	$>41\ 7$ [7]

* Solubility products that were corrected to ionic strength were used for calculation
^{b} Solubility products at I $= 0$ 1 and 0 3 were estimated using the Davies equation [12]
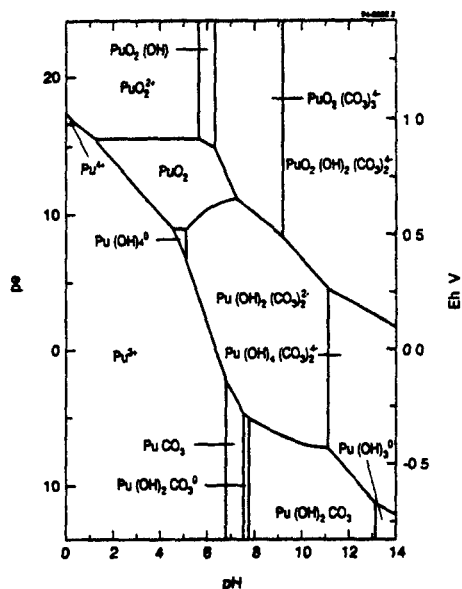

Fig 5. Eh-pH diagram of Pu, total carbonate concentration 4×10^{-3} M

in reference [17] is shown in Fig 5 This diagram is different from previous ones [18, 19], in which the formation of hydroxycarbonate species have not been taken into account

4. Conclusion

The Pu solid phase formed in the present solubility experiments is likely to be $PuO_2 \cdot xH_2O$ Carbonate and bicarbonate have significant effect on the solubility of Pu(IV) Species of $Pu(OH)_2(CO_3)_2^{2-}$ is predominant in bicarbonate solutions, while species of

$Pu(OH)_4(CO_3)_2^{4-}$ is responsible for the solubility in carbonate solutions

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